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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

STUDIES ON FLUORITE.

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I. The Fluorescence of Fluorite.

Although the phenomena of fluorescence have been the object of much research for many years the results obtained in the way of general laws must be called very meagre. The law of Stokes, which appears on closer investigation to have many exceptions, is almost the only generalization with direct bearing on the subject. The other general law, that all substances which fluoresce show selective absorption, is of more general bearing, and may perhaps be deduced directly from fundamental thermodynamic principles.

Dividing the subject matter quite arbitrarily into solids, liquids, and gases, it may be said that in gases only a very few cases of fluorescence have been observed. The fluorescence of sodium vapor, first observed by Wiedemann and Schmidt[1] and lately studied with most interesting results by R. W. Wood,[2] offers at least the possibility of a great increase in our general knowledge of the subject. In gases the factors determining luminescence are probably easier and more amenable to experimental control than in the other states of matter.

Among fluorescent liquids there appears a more or less general possibility of systematization. Certain organic groups or radicals seem to carry with them under definite conditions the power of conferring fluorescence on compounds containing them, and the presence or absence of the property of fluorescence may therefore be prophesied with some certainty from a knowledge of the chemical composition of the substance.

With regard to the phenomena of fluorescence in solids we are without any general laws or relations whatever. Those organic substances which show fluorescence in solution often show it also when dried in gelatine, and sometimes even in the pure solid state; but in the latter case the fluorescence color is usually quite different from that of the same substance in solution.

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[1] Wied. Ann., **57**, 447 (1896).

[2] Phil. Mag. [6], **10**, 513 (1905).

Our present methods of investigation seem inadequate. From the mass of fact which has been gathered it seems possible that fluorescence in solids, and especially in inorganic solids, is determined by the presence of small quantities of impurities, but in the uranium salts and the platinocyanides we have substances which are, according to the usual standards, pure, and which are nevertheless capable of exhibiting strong fluorescence, and organic substances which are pure in the same sense often exhibit this property in the strongest degree. The conclusions which may be drawn from the chemical attacks on the question are few and uncertain, and there are as yet no general principles which can be stated.

The only methods of investigation which have been applied to the problem with the exception of chemical analysis and synthesis are those of spectroscopy.[3] In spectroscopy again we have a multitude of facts with only an occasional connection of narrow scope, and the results which may be hoped for are immediately limited by our limited knowledge of the method itself. There is satisfaction in knowing the spectrum of the light emitted by a fluorescing substance under definite conditions of excitation, and such knowledge has of course scientific value, but any extension of our knowledge of fluorescence based on spectroscopic methods can go but very little farther, since we know practically nothing of the mechanism of spectrum production even in the simplest case. The fundamental problem of the appearance of a fluorescence spectrum goes back to the question how any spectrum is produced, and the complete answer to one of these questions includes the answer to the other.

One general fact appears to hold for every case of fluorescence, and that is *selective absorption* by the fluorescing substance. This substance is able to select from the variety of light vibrations which enter it those of certain definite periods, transforming their energy in part into heat, about the period of which we know very little, and in part into light, which is emitted and which determines the spectrum of the fluorescence. This fact of selective absorption brings with it the conclusion that there is something in the substance which has the power of taking up periodic disturbances of definite period, and with their aid setting up within itself disturbances of the same general nature but usually of different period, which result in the emission of light. It would be comparatively easy to picture resonance of such a character that the absorbed and emitted periods should be the same, but there does not appear to be any experimental evidence that such a case exists. Even in sodium vapor, which is nearest this ideal case, the excited fluorescence light has not exactly the same wave-length under all conditions as the exciting light, as may be seen immediately from Professor Wood's photographs. And when we remember that very frequently luminescence spectra of very nearly the same character are given out by a substance when it is excited by light, heat, kathode bombardment, X-rays, friction, or radium, it is evident that a very general property is involved of which excitation by light vibrations is only a phase.

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[3] For a possible variation see Nichols and Merritt, Phys. Rev., **19**, 396 (1904).

It seems probable that neither chemical analysis nor spectroscopic analysis in its present condition can serve as an adequate tool with which to attack the fundamental problems of fluorescence, yet they are almost the only tools available. Burke's investigation on the change of absorption during fluorescence,[4] and Nichols' and Merritt's work on the change of electrical conductivity of solutions while fluorescing,[5] are suggestions of possible variations in the method of attacking these phenomena.

The present paper contains a brief summary of the spectroscopic results obtained during a study of a single substance — fluorite. This substance is remarkable because of the large number of methods of excitation which may be employed with it and because of the brightness of the luminescence light emitted under the influence of most of these exciting sources.

It is the author's intention to carry the study of light emission by fluorite through the entire series of methods of excitation. The present paper contains data on the fluorescence spectra only; that is, on the light emitted by fluorite when the exciting source is light.[6]

Experimental Data.

The crystals examined were all from Weardale, England. Spectroscopic data on the results of the study of these crystals has already been given in full in the Astrophysical Journal for March, 1905. It has seemed advisable to submit a summary of these and of other results obtained since that paper was published to the American Academy, since succeeding results are to be published in the Proceedings, and the connection between the facts of fluorescence and those obtained from other methods of excitation is a very close one.

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[4] Phil. Trans., **191**, 87 (1898).

[5] Phys. Rev., **19**, 396 (1904).

[6] The spectrum of the light emitted being examined *during* excitation.

In Plate 1, the general appearance and something of the detail of the fluorescence spectra from two crystals of fluorite may be seen. These are crystals which have been numbered 4 and 5, and the cuts show the spectra produced when they are excited by the light from the spark between electrodes of various metals. For the tables of measured wave-lengths reference should be made to the paper in the Astrophysical Journal.[7] The facts exhibited by the tables and the plates may be briefly summarized as follows: —

1. The light of the fluorescence excited in a crystal of fluorite by the light of the condensed spark between electrodes of certain metals shows in its spectrum many sharp lines and narrow bands.

2. A single fluorite crystal is able to emit a very great number of these lines and bands, a part only of which appear under excitation by the spark from one metal, another part under excitation by another metal, and so on. The entire fluorescence spectrum of a fluorite crystal must then be considered the sum of all the lines excited by all the different sparks.

3. Certain lines appear to be common to the fluorescence spectra excited by different sparks. This statement holds true to the limit of accuracy of the measurements on the photographs obtained.

4. Certain of these lines and bands are evidently peculiar to the light excited by a single metal. No error of measurement could account for the differences of distribution of the strong lines in the various spectra emitted by the same crystal under excitation by different sparks.

5. The fluorescence spectrum varies from crystal to crystal, not only in minor points, but even in the strongest lines.

6. Metals having strong lines in the ultraviolet part of the spark spectrum excite extended fluorescence spectra.

7. The exciting source for the sharp lines of the photographs is light between wave-lengths λ 3000 and λ 2000, since it is absorbed completely by a thin layer of glass, but not by a considerable thickness of quartz.

8. The strong sharp lines of the fluorescence spectra lie between λ 5700 and λ 6400. No sharp lines whatever have been observed of shorter wave-length than λ 4700.

9. The lines in these fluorescence spectra do not appear to belong to

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[7] Astrophys. Jour., **21**, 83 (1905).

any known substances, and the fact that the fluorescence spectrum changes completely with a change in the exciting source immediately excludes all ordinary substances from consideration.

10. A change of this sort, i. e. a redistribution of sharp lines in a spectrum, corresponding to a change in an exciting source, is something wholly new in spectrum observations.

11. The possibility of optical resonance has been examined with wholly negative results. No relation between sharp spectral lines in the exciting source (of wave-length between λ 3000 and λ 2000) and the strong sharp lines of fluorescence has been found.

12. There is a sharp strong line at about λ 5735 in the fluorescence spectra excited in the same crystal by the spark between the following terminals: — iron, aluminium, cadmium, magnesium, and tin, and the ultraviolet spectra of these metals are so very different as to exclude any relation between a strong line in all of these spectra and a strong line of the fluorescence spectrum. The possibility of optical resonance is made still more improbable by the fact that the spectrum varies sharply from crystal to crystal with the same exciting source.

13. The possibility is suggested that these sharp lines of fluorescence may be connected with an impurity in the crystal. The fluorites giving sharp lines are colored, and the colored parts form layers or strata in which the fluorescence appears stronger than in the other parts of the crystal. These strata were noted by Stokes as being the seat of the "red fluorescence" which he observed and which is here resolved into sharp lines.

14. Whatever the source of fluorescence, it is completely removed or destroyed by heating the crystal to a temperature above 300°.

15. A crystal which has been so heated may be so regenerated by exposure to light that it will give the broad blue band of fluorescence, but the sharp-line portion of the fluorescence light is not regenerated.

16. Under the exciting influence of sunlight the fluorescence spectrum of these crystals contains only the broad diffuse band from about λ 4800 to about λ 4000, without maxima or minima.

The Absorption of Fluorite.

The absorption and emission of fluorite of various colors have been examined in the visible part of the spectrum by Nichols and Merritt.[8] Their results show that as far as their experiments reach the absorption is slight, and that there are no sharp bands in it. Remarkable is the fact that fluorite, which shows no marked absorption out as far as λ 1200, should be strongly phosphorescent. This is the case with some very pure white plates which are used by Dr. Theo. Lyman in his work on the photography of very short wave-lengths. They show no measurable absorption of a selective sort, and permit the passage of light evenly as far as λ 1200, while they are more strongly phosphorescent under the influence of the spark between metallic terminals than many colored fluorites.

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[8] Phys. Rev., **19**, 18 (1904).

Photographs of my own which extend as far as λ 2100 show no marked absorption and no selective absorption whatever. These facts simply point to the flatness of the absorption curve for this substance, and they are all the more remarkable when we consider the great sharpness and intensity of the fluorescence lines and bands from these same fluorites.

Plate 2 shows three photographs enlarged from small plates like those in Plate 1, and they show very clearly that many of the lines in the fluorescence spectra are equally as sharp as the lines in the comparison spark spectra. Some of these lines occur in groups as doublets and triplets, having all of the characteristics as regards appearance and sharpness which characterize the spectra of incandescent metals and gases.

Figure 1 shows a portion of the fluorescence spectrum of a crystal of fluorite excited by the spark between magnesium terminals. It is especially characterized by three strong lines, one of them very strong indeed.

Figure 2 shows the fluorescence spectrum of the same crystal under the exciting influence of the spark between iron terminals. Beside the strong groups in the yellow, orange, and red, there may be seen in this photograph a large number of lines which are partially obscured by the broad band. That these are not lines which have entered the spectrograph from the light of the spark is proven by the fact that the very strongest spark lines are missing from the fluorescence spectrum. In fact, every line which can be seen in this spectrum is a true line of fluorescence light.

Figure 3 shows the fluorescence spectrum of the same crystal under the exciting influence of the spark between cadmium terminals. A number of lines have in this case been reflected in the crystal through poor adjustment, and these appear in the fluorescence spectrum. The strong triplet λ 5737 to λ 5711 is however made up wholly of fluorescence lines, and the other lines belonging to this spectrum can readily be separated from the spark lines which have crept in. The bands in this fluorescence spectrum have every appearance of being made up of unresolved fine lines just as the ordinary bands in metallic and gaseous spectra are.

These lines of fluorescence have, in fact, all the characteristics of sharp spectral lines, comparable with those of metals.

This result is so important and so wholly at variance with the existing ideas about fluorescence that the whole matter deserves minute investigation, and further study is already under way with the assistance of a grant from the Rumford Fund of the American Academy.

II. The Thermo-luminescence of Fluorite.

The more obvious facts about the thermo-luminescence of substances have been known for a very long time. That many substances emit light on being heated to a temperature far below that of incandescence has been known since the time of Boyle, and some crystals having this property were sent to the French Academy of Sciences in 1724. These were evidently fluorspar crystals, and this substance forms the basis of most of the older experiments on the subject, although long lists of thermo-luminescent substances are to be found in the researches of Wedgwood,[9] Brewster,[10] and Pearsall.[11] Later researches of importance have been carried out by Becquerel,[12] Le Bon,[13] and Wiedemann and Schmidt.[14]

General Facts.

The general facts concerning the production of a thermo-luminescence may be briefly summarized as follows: —

1. Certain minerals (fluorite, diamond, leucophane, apatite, scheelite, etc.) and many artificially prepared sulphides of the alkaline earth metals, as well as many salts, emit light when heated to a temperature below that of incandescence.

2. These substances appear without exception to exhibit fluorescence or phosphorescence, or both, under excitation by light, but many of the most brilliantly thermo-luminescent substances are not at all brilliant in fluorescence or phosphorescence, and many brilliantly fluorescent or phosphorescent substances exhibit no measurable thermo-luminescence.

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[9] Phil. Trans., **82**, 28 (1792). Refers to still older literature.

[10] Edinb. Phil. Journal, **1**, 383 (1819).

[11] Journ. of Royal Institution, **1**, 77 and 267 (1830).

[12] C. r., **112**, 557 (1891).

[13] Revue Scientif., **14**, 289 and 327 (1900).

[14] Wied. Ann., **56**, 201 (1895).

3. The time during which the thermo-luminescence persists appears to be a quite definite function of the temperature of heating. Some phosphorescent sulphides may be exhausted of thermo-luminescence at a high temperature in a few seconds, while the luminescence of a crystal of fluorspar may be either exhausted in a short time (a minute or two) at a red heat or may persist for hours or days with a nearly constant intensity if the temperature be kept at 100°. Measurements of the relation between temperature, time of heating, and intensity of the emitted light are now being made.

4. The temperature at which light begins to be emitted by a substance may be a very low one. Some specimens of chlorophane and certain diamonds (especially Brazilian ones) are so sensitive that they show visible light plainly when warmed by the hand, and many other substances show the effect plainly at temperatures below 200°.

5. In many cases the store of light contained in the substance appears not to become exhausted by heating to a temperature below a certain definite maximum, no matter how long the heating is continued. For after all emission has ceased at the lower temperature, more may be produced by raising the temperature to a higher point, and when the light supply has been exhausted at this higher temperature more light is emitted when the temperature is raised still higher. There appears, however, to be a certain maximum temperature at which all of the store of light in the body is exhausted, and further increase in temperature beyond that point does not result in the production of further luminescence.[15]

6. On standing in the dark, the power to emit light on being heated is not regenerated. This is clearly shown by heating a crystal of fluorite to a definite temperature below the maximum until no further luminescence is visible. If the crystal is now cooled and allowed to remain in the dark, and then brought back to the same temperature as before, no light is emitted. If it is heated to a higher temperature, the luminescence begins again.

7. With respect to the regeneration of the thermo-luminescence by light, various substances show differences so great as to make it certain that there is more than one kind of thermo-luminescence. The phosphorescent sulphides are easily regenerated by a short exposure to light, and this effect would naturally be expected from the method of their prepara-

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[15] Le Bon, Revue Scientif., **14**, 289 and 327 (1900); Becquerel, C. r., **112**, 557 (1891).

tion. The thermo-luminescence of substances of this class depends on something which is not destroyed by the action of heat to such an extent or in such a way that it cannot be reformed under the exciting influence of light. But the thermo-luminescence of fluorite is of a wholly different kind. When the store of light has once been exhausted, it may be in a slight degree recovered under the influence of light, but the light produced by a subsequent heating is not the same as the original thermo-luminescence light. This point will be brought out more clearly in the description of my own experiments.

8. With respect to the regeneration of thermo-luminescent power under the influence of the electric spark, these same differences in the two classes of substances are evident. The alkaline earth sulphides are easily regenerated, probably by the light of the spark rather than by any special electric action. Some fluorites, especially those which are usually called *chlorophanes*, which give a strong green thermo-luminescent light, showing a spectrum which is described in a later part of this paper, cannot be so regenerated that the original light is emitted. The power of emitting light is indeed restored under the excitation of the electric spark, but the light emitted is never the same as that produced during the first heating.[16]

9. Many substances change during heating, so that the light, while in some cases remaining apparently nearly constant in intensity, changes in color during the experiment. Others show a great change in intensity, together with changes in the color of the emitted light. It will be seen later that the spectrum of the light from certain fluorites consists of two distinct parts, one of which persists after the other has practically disappeared; and this fact goes one step toward an explanation of the changes in color during heating.

Experimental Data.

The present paper contains data on the spectra of thermo-luminescence of two distinct varieties of fluorite, — one a "chlorophane" from Amelia Court-House, Va., and the other a common, clear, colorless (or very slightly greenish) specimen from Westmoreland, N. H. Both are slightly fluorescent under excitation by ultraviolet light, the fluorescence being of the usual lavender color common apparently to all fluorites under these conditions, and both are phosphorescent, showing this lavender-colored light for some time after removal from the exciting source. Neither is at all brilliantly fluorescent or phosphorescent under the conditions to which they have been subjected, but both are very strongly thermo-luminescent, the chlorophane emitting a very strong bright green light, easily visible even in a well-lighted room, and the other fluorite emitting a lavender or purple light, not very different to the eye from the light emitted by the same substance in fluorescence and phosphorescence.

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[16] Pearsall, Journ. of Royal Institution, **1**, 77 and 269 (1830).

Spectroscopic examination of the light from the chlorophane shows what appears to be a continuous spectrum with a maximum in the green-yellow. Carefully rested eyes enable some other sharper maxima to be seen, but little detail can be made out.

The light from the other fluorite shows several broad bands of a rather diffuse nature, and superimposed over these some sharper lines can be made out. The broad bands of the two spectra are the source of most of the emitted light, and the sharp lines are much obscured by their presence.

The spectrum of fluorites much like the New Hampshire variety has been described by a few observers. The oldest reference found was in a brief note in Poggendorf's Annalen, "from a letter from Herr Kindt."[17] In this note the broad bands of the thermo-luminescence spectrum are mentioned, and the remark is made that the bands are as strong as the absorption bands in the spectrum of the didymium salts. Later references to the same spectrum are to be found in the researches of Hagenbach[18] and Liveing,[19] both of whom observed the broad bands and give their approximate wave-lengths. No reference to photography or more minute examination of the question has been found.

There are at least three distinct stages in the thermo-luminescence of the chlorophane. At a low temperature (50° to 100°) the light is bright green and strong. After the light has begun to grow dim and the temperature is increased and maintained for some time, a yellowish color of less intensity and short duration takes its place, to be in turn replaced by a weak lavender luminescence at a still higher temperature. This final color is very much like that of the fluorescence under excitation by light.

In the case of the other specimen chosen for examination (the colorless crystal from New Hampshire), no such marked differences in the color emitted at different stages of heating were found, but it is evident that the light produced at higher temperatures, toward the end of the luminescence, is of a deeper purple color than that emitted at lower temperatures. In the research of Pearsall[20] a long list of the various colors emitted by different fluorites at various temperatures and times of heating is given. In this same research the matter of the regeneration by the electric spark is taken up fully, but of course without any use of spectroscopic methods.

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[17] Pogg. Ann., **131**, 160 (1867).

[18] Archiv. de Geneve [2], **60**, 297 (1877).

[19] Proc. Camb. Soc., **3**, 96 (1877).

As has been stated, the chlorophane begins to glow at a low temperature. It reaches its maximum at a point not much above 350°, while the other fluorite requires a higher temperature to start the luminescence, and the temperature must be raised to a slightly higher point to completely exhaust the power of luminescence.

The Photography of the Thermo-luminescent Spectra.

Experimentally, the photography of spectra of luminescences of the intensity of these offers no difficulty whatever. Patience is necessary, since a large amount of material must be allowed to luminesce in front of the slit of the spectroscope, and the time during which a single crystal of fluorite glows brightly is rather short. Exposures of about four hours were required to yield measurable plates. Longer exposures could of course have been made, but the advantage gained would be slight, since the continuous background of diffuse light is so strong that the sharp lines are not much more clearly differentiated than with the shorter exposures. A great advantage would be gained by the use of greater dispersion, as the sharp lines could in this way be brought out while the continuous background remained weak. For this preliminary study, however, the spectrum as a whole is of interest, and the dispersion employed is well suited for the purpose. The spectrograph employed was the wide-angle one which had already done good service in the examination of the fluorescence spectra of these same fluorites.[21]

After discarding mechanical arrangements of the nature of hot revolving plates and dishes, the simplest possible method of exposure was employed. The material was heated in a test tube out of range of the slit until it began to glow. It was then held in front of the slit by hand until the glow from the first heating had begun to grow weak, when it was reheated and brought back in front of the slit, and so on until the luminescence was exhausted. Fresh material was then put through the same treatment, and the process continued throughout the time of the exposure. Later, a small electric furnace was used in the same way; the only advantage which it has over the test tube being the better control of the temperature, and this is in part offset by the difficulty of keeping the brightest luminescence directly in front of the slit. The heated crystals decrepitate, and break up into smaller fragments, and occasionally a heavier explosion than usual blows everything out of the furnace, or at least disturbs the position of the main mass of luminescent material. The test tube, held in the hand, can be turned so that the brightest part is always toward the slit, and in general the cruder method is at least as easy in the end.

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[20] Journ. of Royal Institution, **1**, 267 (1830).

[21] Astrophys. Journ., **21**, 83 (1905).

Spectroscopic Results.

TABLE I.

CHLOROPHANE FROM AMELIA COURT-HOUSE, VA.

Continuous spectrum from violet to red, with maximum in the green-yellow both visually and in the photographs. Superimposed over this continuous band the following lines and narrow bands:

4125	2	diffuse.	4415	5	quite sharp.	5375	5	sharp.
4145	2	"	4457	2	diffuse.	5400		diffuse.
4315	1	"	4525	1	"	5435		"
4325	2	sharp.	4580	5	sharp.	5500		"
4335	1	diffuse.	4630	1	diffuse.	5600		"
4347	10	sharp.	4700	2	sharp.	5700		"
4365	4	diffuse.	5175		diffuse.	5893		sharp.

TABLE II.

Clear, colorless fluorite from Westmoreland, N. H. Underlying diffuse band from green to violet, rather sharply bounded at green end, but shading off in violet. Superimposed over this, and in the yellow and red, the following lines and bands:

4108	1	sharp.	4622	1	diffuse.
4130	2	diffuse.	4658	4	sharp.
4150	2	"	4690	2	"
4192	1	"	4703	2	"
4230	2	"	4715	1	diffuse.
4250	2	"	4770	5	nearly sharp.
4298	1	"	4800	2	"
4312	1	"	4815	3	"
4330	2	"	4840	7	diffuse.

TABLE II. — *continued.*

4347	10	sharp.
4365	5	max. in diffuse band.
4370	2	
4382	2	sharp, in diffuse band.
4398	1	
4415	5	not quite sharp.
4450	1	diffuse.
4462	2	"
4475	1	"
4502	2	"
4540	2	"
4580	4	sharp.
4892	·6	nearly sharp.
4903	5	"
5200 to 5265		broad band.
5375	9	sharp.
5435	4	"
5520	2	"
5720	1	diffuse.
5800	1	"
5893	8	(sodium lines unresolved ?)

TABLE III.

LINES COMMON TO BOTH SPECTRA.

Westmoreland.	Chlorophane.	Mean.	Intensity.	Maximum Error.
4130	4125	4127	2	
4150	4145	4147	2	
4312	4315	4313	1	
4330	4325 4335	4330	2	
4347	4347	4347	10	±2 A. E.
4365	4365	4365	5	±2 A. E.
4415	4415	4415	5	
4462	4457	4460	2	
4580	4580	4580	4	
4625	4630	4627	1	
4690 4703	4700	4700	2	
5375	5375	5375	9	±3 A. E.
5435	5435	5435	4	±4 A. E.
5893	5893 (?)	5893	8	±2 A. E.

In all of the photographs taken magnesium was used as comparison metal, and lines in the luminescence spectrum which fall near sharp magnesium lines can therefore be measured with considerable accuracy. It is on these lines that the values in the column headed "Maximum Error" are based. For example, the line at λ 4347, a sharp strong line in the thermo-luminescence spectrum of each of these fluorites, lies near the λ 4352 line of the magnesium spark spectrum, and the error of measurement on several plates is not greater than the value given. The line at λ 5893 coincides exactly with the unresolved sodium lines in the comparison spectrum.

Plate 3 is a reproduction of a photograph of the thermo-luminescence spectrum of the Westmoreland fluorite, with the comparison spectrum of the magnesium spark beside it. The magnesium spectrum is much over-exposed in this photograph, and the exposure for the luminescence spectrum has been perhaps somewhat too short. A longer exposure brings out the diffuse background rapidly, and the lines are not made easier to measure. The chlorophane spectrum has so much of the continuous background as to make it difficult of reproduction, and doubtless many weaker sharp lines escaped measurement from this same cause.

Conclusions.

It would appear proven that the sharp-line portion of the spectrum from the two fluorites is the same. All of the strong lines agree in wave-length and in relative intensity within the limit of accuracy of the measurements. It should be remarked that "intensity" measurements of lines nearly hidden in the diffuse bands are of little significance, but they have been graded on a scale of 1 to 10 for the purpose of a qualitative comparison.

The diffuse bands of the two spectra are, however, entirely different, and the color of the thermo-luminescence light is determined by the preponderance of one or the other series of diffuse bands, the sharp-line portion being in either case comparatively weak.

The change of color of the luminescence light during the heating can now be explained. It is due to the persistence of one of the sources of luminescence — the one causing the appearance of the sharp lines or the one causing the appearance of the diffuse bands — after the other source has ceased to be active. In the Westmoreland fluorite the sharp lines appear to weaken and disappear before the broad bands, and the same seems to be true of the chlorophane, although the question is more difficult of decision in the latter case. A spectro-photometric study of the rate of decay of the lines and bands is already under way.

All attempts to place the sharp lines to the credit of any known elements have been so far unsuccessful. There are of course many coincidences with lines of well-known substances, especially since the dispersion and the corresponding accuracy of measurement are so small; but the other strong lines of the substance are absent in every case, and one would demand the coincidence of an entire series of lines of an element before admitting that a metal or a gas could show a line spectrum under the conditions of the experiments. The very exact coincidence of the line at λ 5893 with the mean of two sodium lines suggests the possibility that this may be that pair unresolved; but it would seem that resolution into the two constituent lines is the very least that could be demanded before deciding that the sodium pair do actually appear under these circumstances, and any decision on this point should be reserved until this resolution has been accomplished.

There can be no doubt that these thermo-luminescence spectra are composites, and that the sources, whatever they may be, of the parts of the composite, are distinct. One of these sources gives rise to the diffuse band part of the spectrum in each case, and this part is like the usually observed spectra of fluorescence and phosphorescence. It is evidently different in the two fluorites. The other source is capable of giving a spectrum in most respects similar to the sharp-line spectra usually associated with incandescent gases. This source is *common to the two fluorites.*

It seems imperative that as minute an examination as possible of the impurities present in fluorites should be made, to include not only a chemical analysis but also an examination of the gaseous and liquid inclusions in the mineral.

A generous grant from the Rumford Fund of the American Academy of Arts and Sciences has been of much aid in this work, and a continuance of the investigation in several directions is already under way.

III. GASEOUS AND LIQUID INCLUSIONS IN FLUORSPAR.

Many facts connected with the various phenomena of luminescence in the mineral fluorspar point to the possible influence of impurities of a gaseous or liquid nature, which are usually present as inclusions, and which are driven out or decomposed when the mineral is heated. There is a very general impression that these impurities exercise a determining influence in the emission of light by the substance,[22] and especial weight has often been laid on the analogy with the necessary presence of small quantities of impurities (usually copper, bismuth, or manganese, and a salt of sodium or potassium) in order that phosphorescence shall be exhibited by the sulphides of calcium, barium, and strontium. Since most colored minerals lose their color, their power of fluorescing and phosphorescing, and their content of included gases at about the same temperature and after about the same duration of heating, a direct connection between these three properties has often been suggested, and a relation of this kind is usually accepted as a probability by every one who studies the phenomena in question.

Spectroscopic investigations on the fluorescence and thermo-luminescence of the mineral fluorspar have yielded many facts of interest, and several new and wholly unexpected discoveries.[23] It seems necessary to examine the included gases and liquids and the other impurities in the naturally occurring mineral as minutely as possible, with especial reference to some chemical factor which might exert an influence on the luminescence phenomena.

The Color of Minerals.

The mineral fluorite is remarkable for the variety of colors which it may exhibit. It occurs in fact in nearly every color of the entire spectrum, with the possible exception of bright red, and not only do fluorites from different localities show this difference in color, but even the most homogeneous and perfect crystal often shows a series of layers of different colors sharply separated from each other, and usually lying in planes parallel to the natural faces of the crystal. The same crystal often shows as many as four or five sharp differences in color, and the colored strata often repeat in sets in which the colors take different sequences until the number of visible separate layers reaches twenty or more. Sir David Brewster[24] was the first to call attention to this structure of fluorite, and even at that early date he suspected a relation between these strata and the remarkable phenomena of fluorescence which he was investigating.

The general question of the cause of color in minerals has been made the subject of a great deal of investigation, without any satisfactory or final answer having been reached. Two diametrically opposite opinions still exist, — one, that the color of many minerals, fluorite among them, is due wholly to the presence of organic coloring materials,[25] the other, that there is no sufficient proof for this opinion.[26] The method of study in all of these researches was the one which suggests itself immediately, — heating the mineral until the organic substances present are driven off or decomposed, and collecting the gases and the liquid distillate when any are produced.

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[22] See Becquerel, C. r., **112**, 557 (1891).

[23] See the two preceding divisions of this paper.

[24] Edinb. Phil. Trans., **16**, [2], 111 (1812) ; Edinb. Jour. Sci., **6**, 115 (1821).

Wyrouboff[27] was the first to make a categorical statement in the matter. He heated minerals in a current of oxygen and determined the resulting carbon dioxide and water, finding from his experiments that the amount of carbon and hydrogen found in the analyses was nearly proportional to the intensity of the color of the mineral. These experiments were especially on fluorspars from different localities and of different colors, and his decision was that the colors were *organic.* Foerster[28] repeated these experiments on a number of fluorites and showed that the quantities of hydrogen and carbon produced are not by any means proportional to the intensity of color in the mineral, clear white specimens often showing as large an amount of organic impurity as the most deeply colored. My own analyses confirm these results of Foerster's in every way, but it does not by any means follow from these results that the coloring substances are not organic. The only conclusion which seems to me justified is that the other crystals contain organic substances which are not colored. At a much later date Weinschenck[29] made an exhaustive series of analyses to determine the same question, arriving at the conclusion opposite to that of Wyrouboff, and a little later Kraatz and Wöhler[30] arrived at the opposite result from an equally careful series of analyses. The question as to the cause of the color of fluorspar still remains in this unsettled state.

The Odor of Fluorspar.

Another peculiarity of fluorspar from many sources, and one which might perhaps be expected to throw some light on the source of its luminescences, is the very strong odor which is produced when the mineral is heated or ground to powder in a mortar. Schafhäutl[31] showed that chlorine monoxide is produced when the famous fluorite from Wölsendorf is heated. Schönbein, Meissner, Schrötter,[32] and others were of the opinion that the odor produced on heating is due to ozone. Becquerel and Moissan[33] found traces of free fluorine in the gases distilled from some fluorites, and ascribe the odor to this substance. The great majority of all the analyses of the mineral show the presence of small but appreciable quantities of chlorine.

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[25] Wyrouboff, Bull. Soc. Chim., **1866**, 334; Kraatz and Wöhler, see Ztsch. für Min. u. Cryst., **33**, 632 (1900).

[26] Weinschenck, Ztsch. anorg. Chem., **12**, 375 (1896); Foerster, Pogg. Ann., **143**, 173 (1879).

[27] Bull. Soc. Chim., **1866**, 334.

[28] Pogg. Ann., **143**, 173 (1879).

[29] Ztsch. anorg. Chem., **12**, 375 (1896).

[30] See Ztsch. für Min. u. Cryst., **33**, 632 (1900).

The odor of all the samples of fluorite which I have examined by heating is what would be called distinctly "empyreumatic" — closely resembling the odor arising from the distillation of wood, and certainly of organic origin. None of the many samples which have been at my disposal have shown any very marked odor on attrition, but a few give an "earthy" odor, not very characteristic, but suggestive of organic origin.

Inorganic Impurities.

The most general of these appear to be chlorine, iron, and phosphoric acid, neither of which is a perfectly general impurity, and neither of which is usually supposed to exercise any influence on luminescences. Not long ago Humphreys[34] showed that yttrium is an almost universal impurity in fluorite, using the delicate spectroscopic test for the presence of this strange element. For the present, attention has been confined to those substances which can be volatilized or decomposed by a low red heat, and yttrium compounds would not be included, though the presence of this substance is certainly suggestive.

Gaseous and Liquid Inclusions in Minerals.

These have been the subject of much investigation since the discovery of carbon dioxide in liquid form in crystal cavities by Brewster.[35] While carrying out this investigation he found that air and water are present in certain fluorites, and since that time carbon dioxide, hydrogen, nitrogen, carbon monoxide, oxygen, and hydrocarbons have all been reported as existing in the form of inclusions in this mineral. Tilden[36] and Gautier[37] examined the gases produced by heating many rocks and minerals, with especial attention to the probable conditions of temperature, pressure, and concentration of water vapor which existed on the earth at the time the minerals were formed, and they suggest reactions between water vapor, carbon dioxide, and the ferrous compounds of the rocks and minerals to explain the appearance of the gases evolved. Ramsay and Travers[38] also examined a number of minerals with the same object in view.

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[31] Liebig's Ann., **46**, 344 (1843).

[32] Pogg. Ann., **111**, 561 (1860).

[33] C. r., **111**, 669 (1890).

[34] Phys. Rev., **19**, 300 (1904).

[35] Edin. Trans., **10**, 1 (1826).

[36] Roy. Soc. Proc., **60**, 453 (1896).

[37] Bull. Soc. Chim., **25**, 402 (1901).

It is evident that two important questions are involved, — whether or not the permanent gases can remain as such as inclusions in minerals, and whether any conclusions as to the conditions existing on the earth at the time the minerals were formed can be drawn from the inclusions present in them. Travers[39] shows that it is doubtful whether carbon monoxide, nitrogen, oxygen, and hydrogen can remain for a long time included in cavities in minerals, and suggests that they may be formed during the examination of the minerals as a result of the methods of analysis. He shows that many minerals which yield both carbon monoxide and carbon dioxide on being heated give only carbon dioxide when the same mineral is decomposed by the action of an acid.

Direct evidence on this point may be found in the analyses of Hüttner,[40] who heated a number of minerals to 800°–850°, driving out air by means of carbon dioxide and carrying the products of reaction along into the receiving apparatus by means of the same gas. Hüttner expresses the opinion that the hydrogen which he finds in all of his analyses is formed by the reaction suggested by Gautier, i. e., by the action of the ferrous and manganous compounds of the mineral with the water vapor which is always present, and he further offers the opinion that the carbon monoxide found results not merely from the reaction between carbon dioxide and the ferrous compounds, as suggested by Gautier (l. c.), but rather from the direct reduction of carbon dioxide by hydrogen resulting from the above reaction. Travers's conclusion that no carbon monoxide is produced when the mineral is decomposed by the action of an acid is confirmed by Hüttner's results obtained by the same method.

In the special case of fluorite no extended series of analyses of the included gases has been made. The very great difficulties involved in the decomposition of this mineral by an acid and collecting the gases evolved practically excludes this means of deciding whether the gases found exist as such in the crystals or are formed during the progress of the analysis at the temperature necessary for the setting free of the included substances. There are, however, a number of points in previous researches which fall within our general knowledge of chemical equilibrium, and it is the purpose of the present paper to discuss these and to add some new experimental evidence in the matter.

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[38] Roy. Soc. Proc., **60**, 442 (1896).

[39] Ibid., **64**, 130 (1898).

[40] Ztsch. anorg. Chem., **43**, 8 (1905).

The Equilibrium $CO_2 + H_2 \rightleftarrows CO + H_2O$.

The fundamental conclusion which Hüttner draws from his results is that the carbon monoxide which he finds is formed at the temperature of the experiment by the action of hydrogen on carbon dioxide. Now the results of all the investigations on the water-gas equilibrium show that the equilibrium constant

$$K = \frac{C_{CO_2} \cdot C_{H_2}}{C_{CO} \cdot C_{H_2O}}$$

is about unity at 800°; that is to say, at this temperature carbon monoxide and hydrogen are equally strong reducing agents and carbon dioxide and water vapor are equally strong oxidizing agents. At lower temperatures carbon monoxide is the stronger reducing agent, while at higher temperatures hydrogen is stronger.[41]

The results of experiments on this equilibrium have shown that under ordinary conditions, where the gases are simply mixed together in a vessel, the reaction

$$CO_2 + H_2 \rightarrow CO + H_2O$$

has not a measurable velocity at 900°. Hoitsema[42] used the most sensitive tests for carbon monoxide, but could find no trace of this gas even after hours of heating of the reacting mixture at 900°. Hahn[43] found the presence of a great surface of platinum necessary to cause the reaction to reach equilibrium even in the space of many hours. It is of course possible that the minerals themselves act as catalyzers for the reaction, but even if equilibrium were completely reached during the progress of the experiment the relative amounts of hydrogen, carbon dioxide, carbon monoxide, and water vapor found in my experiments cannot possibly be represented by the reaction which Hüttner assumes to be fundamental.

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[41] Hahn, Ztsch. phys. Chem., **44**, 541 (1903).
[42] Ztsch. phys. Chem., **25**, 686 (1898).
[43] Ibid., **44**, 541 (1903).

Experimental Arrangements.

The present series of experiments consisted only in heating fluorite in a vacuum and making a complete analysis of the gases evolved at various temperatures, varied from about 250° to 700°. Samples of gas were pumped out at various stages of the heating and the gases corresponding to the reaction (whatever it may be) at various temperatures for the same specimen of fluorite were separately analyzed. For the lower temperatures the mineral was heated in a glass or porcelain retort or a glass or porcelain tube in an air bath. For the higher temperatures the fluorite was heated in a porcelain tube in a combustion furnace, and the temperatures are therefore only rough approximations. The retort or tube was connected with a cooled receiver in which the liquid distillate condensed, and beyond the receiver with a Toepler vacuum pump of the form usual for the collection of gases. The gases were collected over mercury at the delivery end of the pump, and passed into the usual apparatus for gas analysis wholly through sealed glass connections. For the determination of the rare gases a second Toepler pump was connected with the first through a series of combustion furnaces containing reagents necessary for the removal of nitrogen. The purified residue was finally passed through the second pump into a Geissler tube for spectroscopic examination. In order to obtain a sufficient quantity of gas for an accurate test for helium, argon, etc., a large quantity of fluorite (10 kilos) was heated in an iron retort and the total residue of the whole volume of gas obtained (about 7 liters) was sent through for the final spectroscopic examination.

The usual weight of fluorite taken for an analysis was 250 gms. and the amount of gas obtained from this amount of the mineral varied greatly. Some of the colored and not very transparent Weardale fluorites yielded as high as 500 c.c. of gas for this amount of material, while other clearer specimens from the same locality gave as low as 50 c.c. Some American fluorites having a deep green color gave only about 20 c.c. of gas, even when they were heated to 700°.

The vacuum reached before heating began was usually about 1 mm. At ordinary temperatures no diminution in the vacuum, such as would be caused by the escape of gas from cavities, was observable after 24 hours.

Analyses of the Gases from Fluorites.

The following are characteristic sets of analyses from a few of the twenty samples analyzed. The results obtained on different samples of the same origin are all of the same order, the percentages varying only within the limit of error of the analytical methods employed.

1. Weardale (England) fluorite. Purple in color. Not very transparent. Contains many inclusions visible under the microscope. Amount taken for analysis, 250 gms. Gas evolved, 320 c.c. Temperature of heating, 280°. Time of heating, four hours. Water produced, 2.4 c.c. 85.3 c.c. taken for analysis.

Composition:

Carbon dioxide	46.7 %
Oxygen	2.9 "
Carbon monoxide	16.7 "
Hydrogen	18.6 "
Nitrogen (remainder)	15.2 "
	100.1 "

2. Same sample. 250 gms. Gas evolved, 280 c.c. Temperature, low red heat (about 650°). Time of heating, two hours. Water, 3 c.c.

Composition:

Carbon dioxide	42.9 %
Oxygen	2.0 "
Carbon monoxide	21.7 "
Hydrogen	16.4 "
Nitrogen (remainder)	16.4 "
	99.4 "

3. Perfectly clear Weardale fluorite crystal. Contains only very minute inclusions, and only a few of these. Deep purple color, slightly brownish. 200 gms. Gas evolved, 68.5 c.c. Temperature, 340°. Time of heating, five hours. Water, about 1 c.c.

Composition:

Carbon dioxide	65.3 %
Oxygen	0.8 "
Carbon monoxide	2.0 "
Hydrogen	26.4 "
Nitrogen (remainder)	4.7 "
	99.2 "

4. Sample from same specimen as 1 and 2, but taken at low red heat and consisting only of the last portions of the gas which came off.

Composition:

Carbon dioxide	64.7 %
Oxygen	0.7 “
Carbon monoxide	12.8 “
Hydrogen	14.8 “
Nitrogen (remainder)	8.0 “
	101.0 “

5. Average analyses of six samples of Weardale fluorites. These were not clear and contained many inclusions. The large amount of carbon dioxide is probably due in part to adhering small particles of calcite, although great care was taken in separating the visible calcite as thoroughly as possible.

(a) Temperature, 28° (air bath)

Carbon dioxide	50 %
Oxygen	2 “
Carbon monoxide	6 “
Hydrogen	14 “
Nitrogen	28 “

(b) At low red heat (combustion furnace)

Carbon dioxide	50 %
Oxygen	1 “
Carbon monoxide	5 “
Hydrogen	16 “
Nitrogen	28 “

6. (a) Clear deep green fluorite from Westmoreland, N. H. No inclusions visible with the microscope. 250 gms. Gas evolved, 18.9 c.c. Low red heat (combustion furnace). Time of heating, four hours.

Composition:

Carbon dioxide	10.0 %
Oxygen	6.3 “
Carbon monoxide	6.9 “
Hydrogen	51.7 “
Nitrogen (remainder)	24.6 “
	99.5 “

(b) Same. Temperature, 260°. Gas evolved, 13.2 c.c.

Composition:

Carbon dioxide	9.2 %
Oxygen	4.7 "
Carbon monoxide	6.6 "
Hydrogen	51.9 "
Nitrogen (remainder)	29.0 "
	101.4 "

The analytical methods were as follows: — Carbon dioxide by absorption in caustic potash; oxygen by alkaline pyrogallate; carbon monoxide by copper ammonium chloride, and from the explosion results; hydrogen by explosion with pure oxygen; nitrogen as remainder, subject to check of more minute analyses of the rare gases. Unsaturated hydrocarbons were tested for by bromine water. Hydrocarbons of the marsh-gas series would have shown themselves in the combustion results if present.

The test for the gases of the helium group was made on the whole amount of gas from about 10 kilos of fluorite. This volume of gas (about 7 liters) was freed from carbon dioxide by collecting it over caustic soda solution, and then put through the regular purification process as given by Travers[44], finally passing over metallic calcium in a series of combustion furnaces. The residue was then subjected to the action of the spark for some time, and the very small quantity of gas remaining was sent on into the spectrum tube through the second pump, which had previously been used to obtain a vacuum in the Geissler tube. The volume of gas remaining after purification was somewhat less than 2 c.c., and this showed only lines of nitrogen and hydrogen, without any indication of the gases of the helium group. A further purification of this residue resulted in its practical disappearance. It was expected that argon would be present, but no lines of this element were observed. A careful test for helium in fluorite has been made by J. Thomsen with negative results.[45]

The Liquid Distillate.

This consists practically entirely of water, although it is brown in color in every case and has a very strong "empyreumatic" odor. It boils at 100° exactly, and gives nothing but water on fractionation.

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[44] The Experimental Study of Gases (1901).

[45] Ztsch. für phys. Chem., **25**, 114 (1898).

Discussion of Results.

As will be seen immediately from the analyses and the corresponding temperatures, there can be no question of the formation of the carbon monoxide in the way which has been suggested by Hüttner. These temperatures are all so low that even if equilibrium had been reached at the temperature of the experiment, which is not at all probable, nothing like the required concentrations of carbon monoxide could result. In fact, in some of the analyses the carbon monoxide equals in concentration the hydrogen, and the relations of the gases are such as would correspond to equilibrium at a temperature above 1000°. Nor can any concentration of the water vapor, which is present in concentrations of the same order as those of the other substances, explain any such results. It seems equally improbable that the carbon monoxide should have been formed from carbon dioxide at any time in the history of the mineral, since the presence of these volatile coloring matters proves that the temperature of the mineral has never been higher than 300°, at which point the color is completely discharged.

There can be no doubt whatever as to the existence of organic substances in these fluorites. The brown substance which comes over with the water in the distillate can be extracted with ether, and is evidently a product of destructive distillation. I see no reason whatever to question the statement that the color of the fluorites is due to organic coloring substances. It is perfectly true that there is no relation between the intensity of color in a crystal of this mineral and the amount of carbon and hydrogen found in the analyses. I have examined some perfectly clear white samples which gave a great deal of gas per weight of substance. But it seems to be just as reasonable that certain of these organic substances should be *colorless* as that they should be anything else, and in the light of this idea all of the conflicting conclusions drawn from the analyses of the past forty years can be easily understood and reconciled.

The Cavities in Fluorite.

Microscopically examined, all sections of these fluorites, with the exception of some very homogeneous and clear ones, show many small cavities, each containing liquid and gas. In some cases the distribution of these cavities follows the colored stratified structure of the crystal, but in others the distribution appears to be wholly irregular. The number of these cavities appears to bear no relation whatever to the intensity of the color, for some of the whitest and clearest crystals have the largest number of cavities, and some deeply colored green and purple ones are almost wholly free from them. The change in appearance of some of these deeper colored crystals, on being heated, is a very marked one: the colored strata become milky and opaque, and lose their color completely at a temperature not far above 300°. Those parts of the crystal which were previously uncolored remain perfectly clear and show not even a trace of milkiness. Other crystals, especially those o yellow or green coloring, are comparatively without stratification, and so far as the experiments have shown, these are the ones which yield but little gas on being heated.

Conclusion.

Although many facts brought out during the study of the fluorescence and thermo-luminescence of fluorite appear to point toward impurities which might determine the luminescence, the present examination of the gaseous products obtained by heating these same fluorites *in vacuo* reveals nothing out of the ordinary among the constituents of the mineral. The analyses have only confirmed what was already known; that is, that practically all fluorites contain organic materials. The old question as to the cause of the color is of course not definitely settled by these experiments, which show only that color, gas content, and fluorescence disappear at the same temperature, and that the gases produced while the color is disappearing are such as would be obtained from an organic distillation of a destructive sort. Taking into account the accurate work of other observers, the necessary conclusion seems to be that the hydrogen, carbon dioxide, and carbon monoxide which are produced when fluorspar is heated are the result of the decomposition of some organic coloring substance which is present in the mineral. Oxygen and nitrogen are in no case present in these analyses in the proportions in which they exist in air, and this suggests that the greater part of the oxygen has been used up to form carbon dioxide and water, whether during the progress of the analyses or not cannot be directly decided.

No proof whatever that these organic substances have anything to do with the fluorescence and thermo-luminescence of these crystals has been found. In fact, the regeneration of a part of the thermo-luminescence power of chlorophane, described in the preceding section of this paper, seems to indicate an inorganic source for at least a part of the emitted light.

The results of this investigation may be considered wholly negative, in so far as the explanation of the facts of luminescence in the mineral fluorite is concerned. It has, however, seemed a very necessary step in the series of investigations which is now being carried on with the generous aid of the Rumford Fund. It permits attention to be turned toward other questions with a sense of at least having looked in this direction for the mysterious source of the luminescence phenomena in this substance, fluorite.

Jefferson Physical Laboratory,
Harvard University,
Dec. 27, 1905.

EXPLANATION OF PLATE 1.

FIG. 1. Fluorite crystal No. 5. Magnesium spark as exciting source.

FIG. 2. Same crystal and spark, with inductance in the secondary discharge circuit.

FIG. 3. Same crystal. Iron spark.

FIG. 4. Same as No. 3, with inductance in secondary circuit.

FIG. 5. Fluorite crystal No. 4. Iron spark.

FIG. 6. Fluorite crystal No. 5. Cadmium spark.

FIG. 7. Fluorite crystal No. 4. Cadmium spark.

FIG. 8. Fluorite crystal No. 5. Aluminium spark.

FIG. 9. Same, with inductance in secondary circuit.

FIG. 10. Fluorite crystal No. 4. Aluminium spark.

FIG. 11. Fluorite crystal No. 4. Zinc spark.

FIG. 12. Fluorite crystal No. 5. Arc between carbon terminals as exciting source.

In each photograph the exciting spark forms the two outer spectra and the fluorescence spectrum is in the middle.

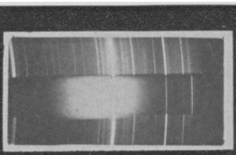

FIG. 1.

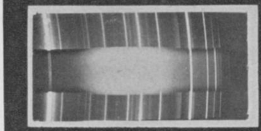

FIG. 2.

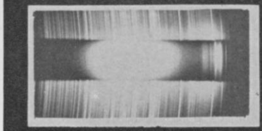

FIG. 3.

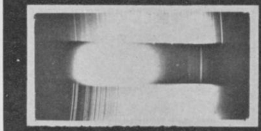

FIG. 4.

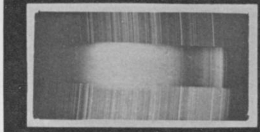

FIG. 5.

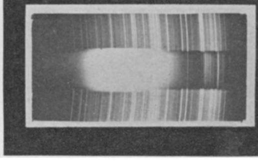

FIG. 6.

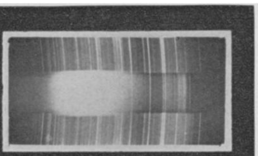

FIG. 7.

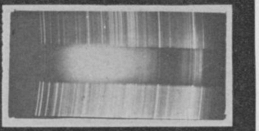

FIG. 8.

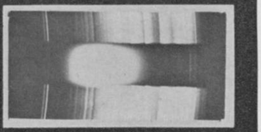

FIG. 9.

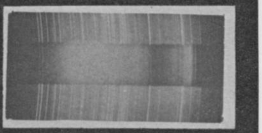

FIG. 10.

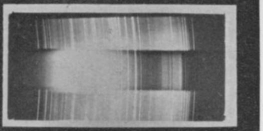

FIG. 11.

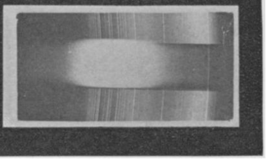

FIG. 12.

EXPLANATION OF PLATE 2.

FIG. 13. Fluorescence spectrum of fluorite excited by magnesium spark. Magnesium comparison spectra.

FIG. 14. The same crystal excited by iron spark. Iron comparison spectra.

FIG. 15. The same crystal excited by cadmium spark. Cadmium comparison spectra.

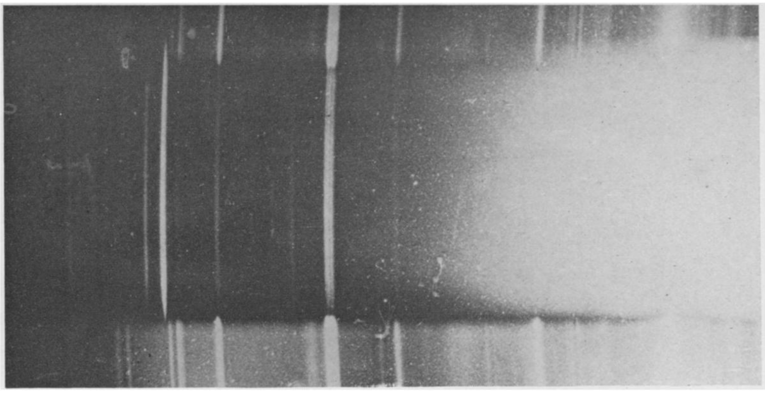

FIG. 13

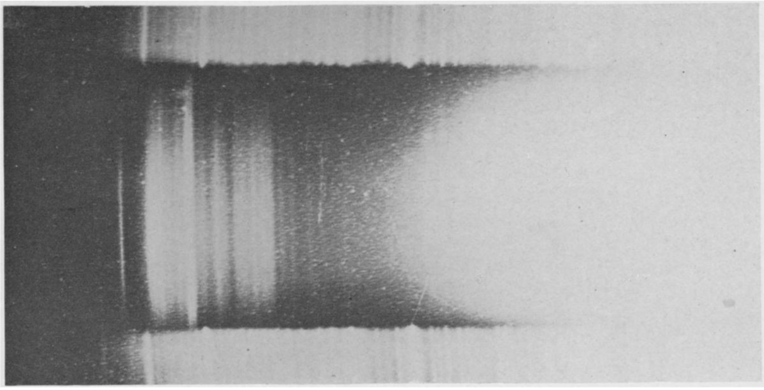

FIG. 14.

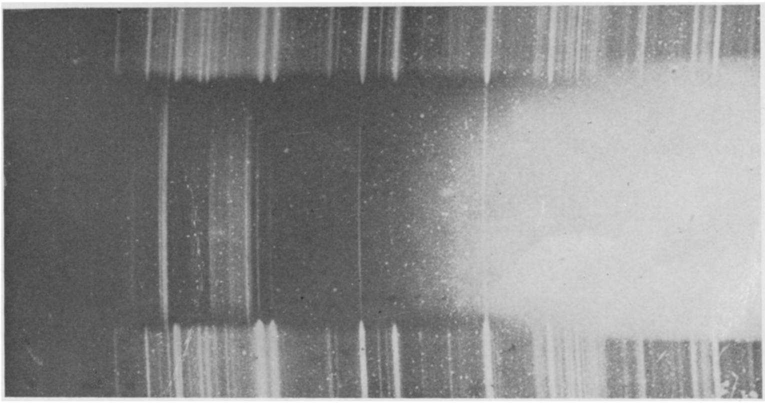

FIG. 15.

EXPLANATION OF PLATE 3.

Fig. 16.

The upper spectrum is the spectrum of the luminescence produced in a piece of fluorspar by heating it to about 200° C. The lower spectrum is that of the magnesium spark.

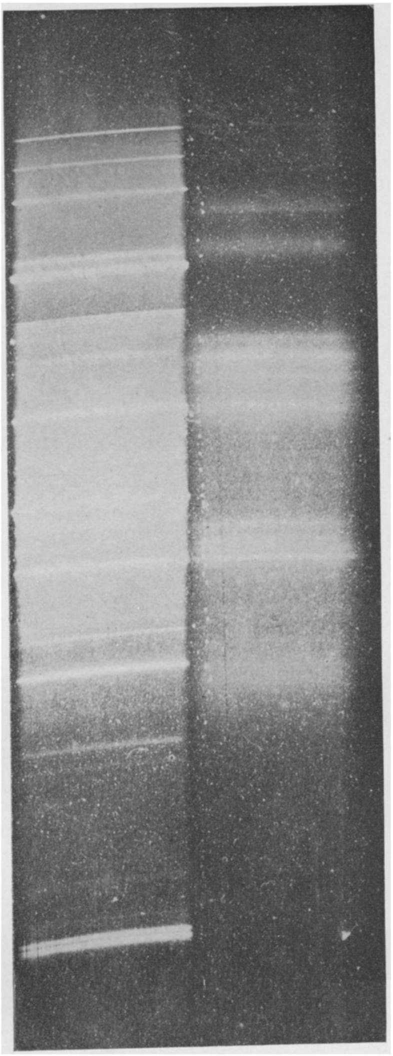

FIG 16.